Supplementary Information

Tunable Silicone Elastomers through PDMS Ring Network Design and Post-Curing Chemistry

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Table S1. Sample names and corresponding details.

Sample names	Description
DMS-H11	Hydride-terminated PDMS with $Mn \approx 1200$ g mol^{-1}
DMS-H21	Hydride-terminated PDMS with $Mn \approx 6100$ g mol^{-1}
HMS-301	Hydride-terminated PDMS with $Mn \approx 1900$ g mol^{-1}
DMS-V31	Vinyl-terminated PDMS with $Mn \approx 18000$ g mol^{-1}
DMS-DT	Dual-functional prepolymer of PDMS (DMS-H11) functionalised with 1,5,9-decatriene
DMS-DT-H11	A concatenated ring elastomer prepared from DMS-H11 and DMS-DT.
DMS-DT-H21	A concatenated ring elastomer prepared from DMS-H21 and DMS-DT.
Reference	Reference elastomer prepared from DMS-V31 and HMS-301 using conventional crosslinking.

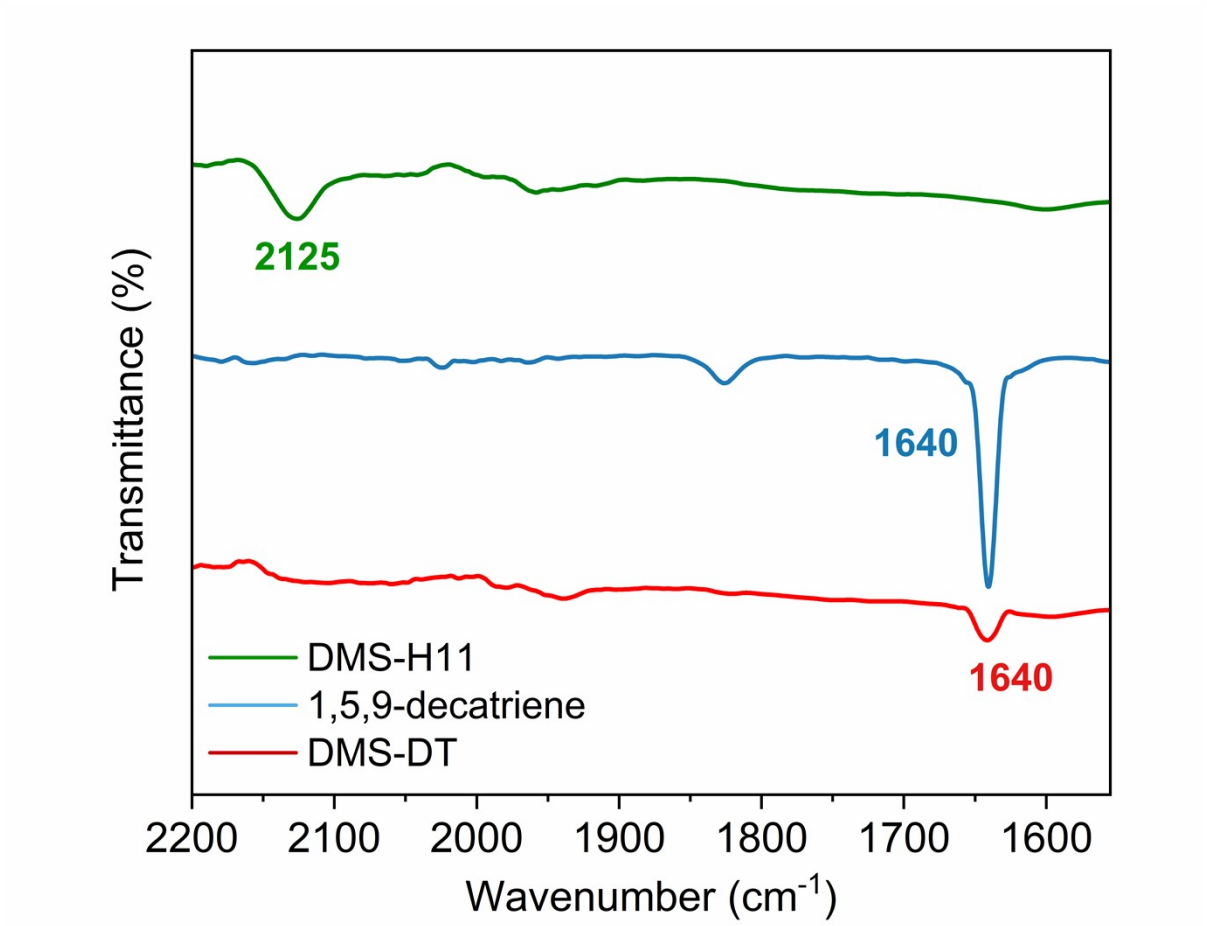


Figure S1. FT-IR spectra of hydride-terminated PDMS, DMS-H11 (green, top curve), 1,5,9-decatriene (blue, middle curve), and DMS-DT prepolymer (red, bottom curve).

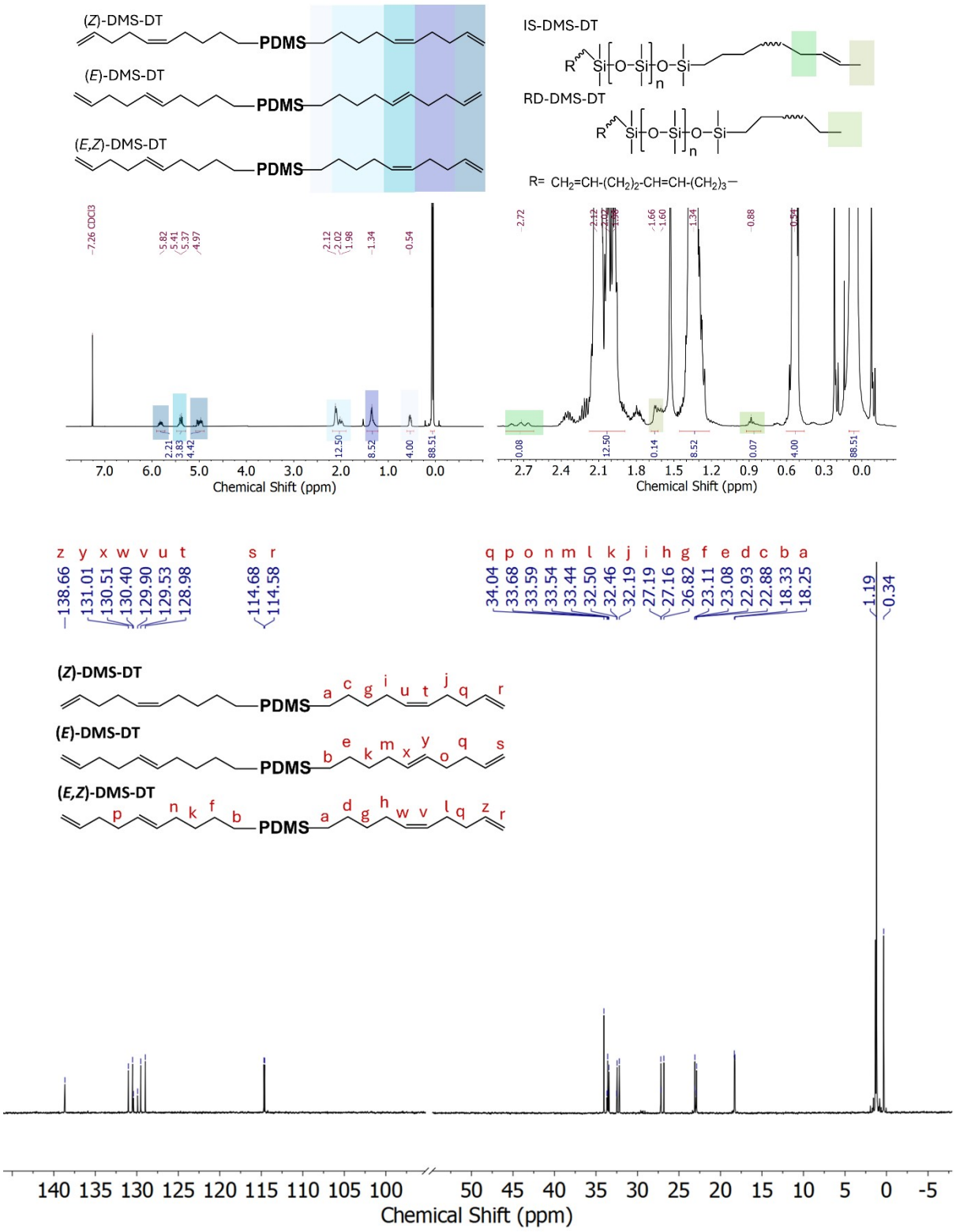


Figure S2. Top: ^{1}H-NMR spectra of the DMS-DT prepolymer, with resonance peaks assigned to the hydrosilylation products (left spectrum), the reduced product (RD), and the isomerized product (IS) identified (right spectrum). Bottom: ^{13}C-NMR spectra of the prepolymer DMS-DT.

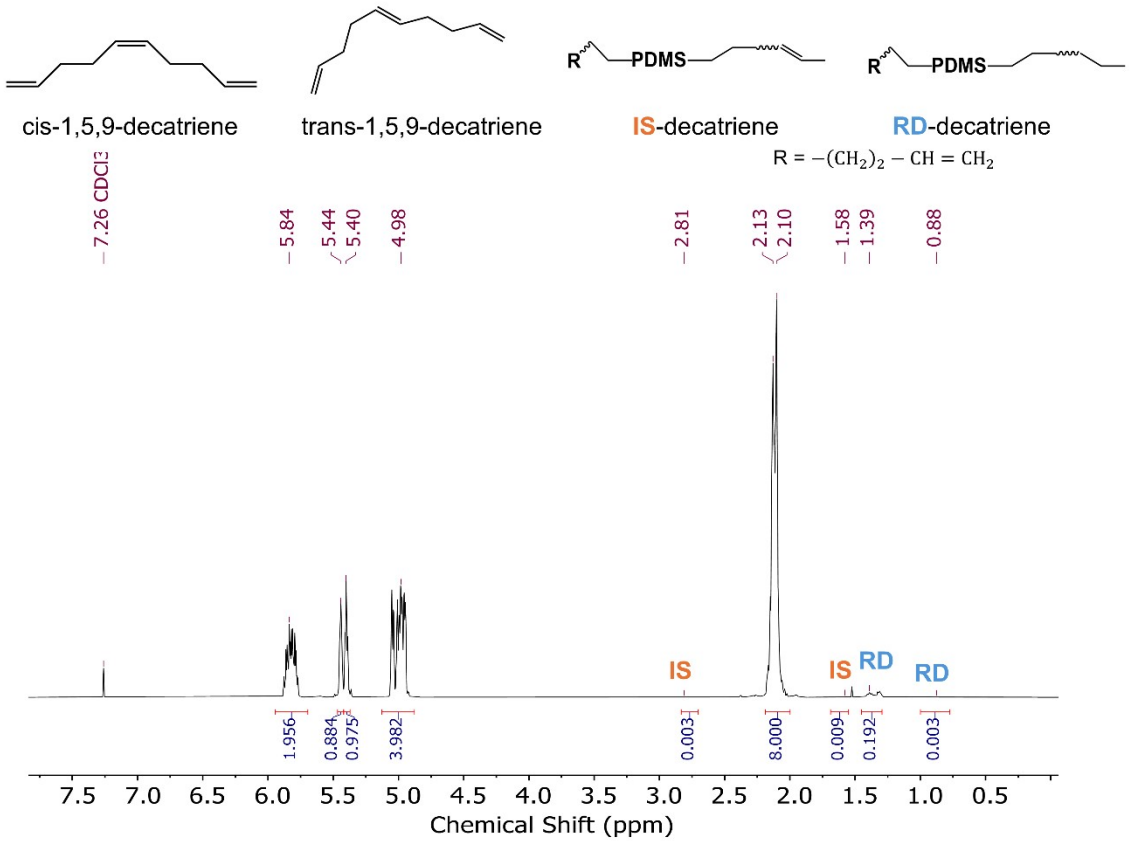


Figure S3. ^{1}H-NMR spectrum of the 1,5,9-decatriene precursor, showing the assigned resonances corresponding to the cis- and trans-isomers, the reduced-vinyl group (RD-decatriene), and the isomerized-vinyl group (IS-decatriene).

The ^{1}H-NMR (400 MHz, $CDCl_3$, δ_H) of the 1,5,9-decatriene shows the resonances at: 4.98, 5.84 ppm (C***H*****$_2$**=CH-); 5.44 ppm (C***H***=C***H***, trans-isomer); 5.40 ppm (C***H***=C***H***, cis-isomer); 2.13, 2.10 ppm [C***H*****$_2$**-C***H*****$_2$** (cis, trans-isomers)]; 2.81, 1.58 ppm (IS-decatriene); 1.39 and 0.88 ppm (RD-decatriene).

Table S2. Composition (%) of the 1,5,9-decatriene precursor.

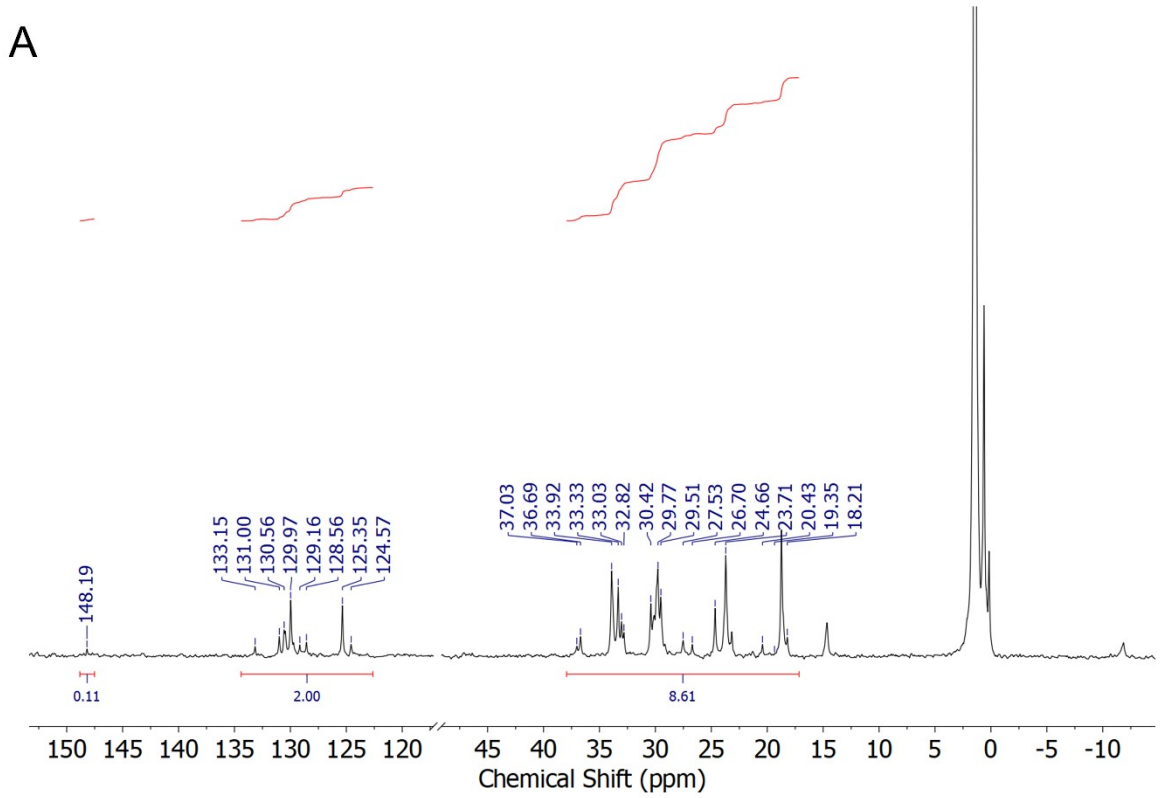
Identified structure	**Composition (%)**
IS-decatriene	1.44%
RD-decatriene	0.09%

Table S3. Prepolymer DMS-DT composition ratios. RD is the prepolymer with the reduced-vinyl group, while IS is the prepolymer with the isomerized-vinyl group.

	Product ratio (%)					
Reaction product no.	(*Z*)-DMS-DT	(*E*)-DMS-DT	(*E,Z*)-DMS-DT	RD-DMS-DT	IS-DMS-DT	Reaction Yield (%)
1	43	48	7	1	1	96
2	41	47	9	2	1	98
3	40	44	9	4	3	96
Average	41	46	8	2	2	97

Table S4. Molecular weight and polydispersity index (PDI, M_w/M_n) obtained from SEC and ^{1}H-NMR for the prepolymer DMS-DT.

Entry	**M_w (SEC) (g mol^{-1})**	**M_n (SEC) (g mol^{-1})**	**PDI (SEC)**	**M_n (^{1}H-NMR) (g mol^{-1})**
1	3155	2147	1.47	1566
2	3234	2197	1.47	1567
3	3125	2196	1.42	1568
4	2847	2078	1.37	1522
5	3060	2167	1.41	1522



The ^{13}C-NMR (400 MHz, $CDCl_3$, δ_C) resonances at 18.21 ppm (1), 18.73 ppm (8), 20.43 ppm (34 + 41 + 49 + 55), 23.16 ppm (14), 23.71 ppm (2 + 9), 24.66 ppm (42), 26.70 ppm (3), 27.53 ppm (4), 29.51 ppm (29 + 31 + 32 + 39 + 47 + 53), 29.77 ppm (30 + 38), 30.12 ppm (30 + 38 + 42), 30.42 ppm (34), 32.82 ppm (10 + 17 + 40 + 52 + 60 + 57 + 58), 33.03 ppm (33 + 37 + 48 + 54), 33.33 ppm (11 + 29), 33.92 ppm (18), 36.69 ppm (25), 37.03 ppm (49), 124.57 ppm (27 + 56), 125.35 ppm (35), 128.56 ppm (36 + 43 + 50 + 59), 129.16 ppm (5), 129.16 ppm (15 + 16), 130.56 ppm (13 +19), 131.00 ppm (12 + 20 + 44 + 51 + 59), 133.15 ppm (22 + 24 + 26 + 56), 148.19 ppm (21 + 23).

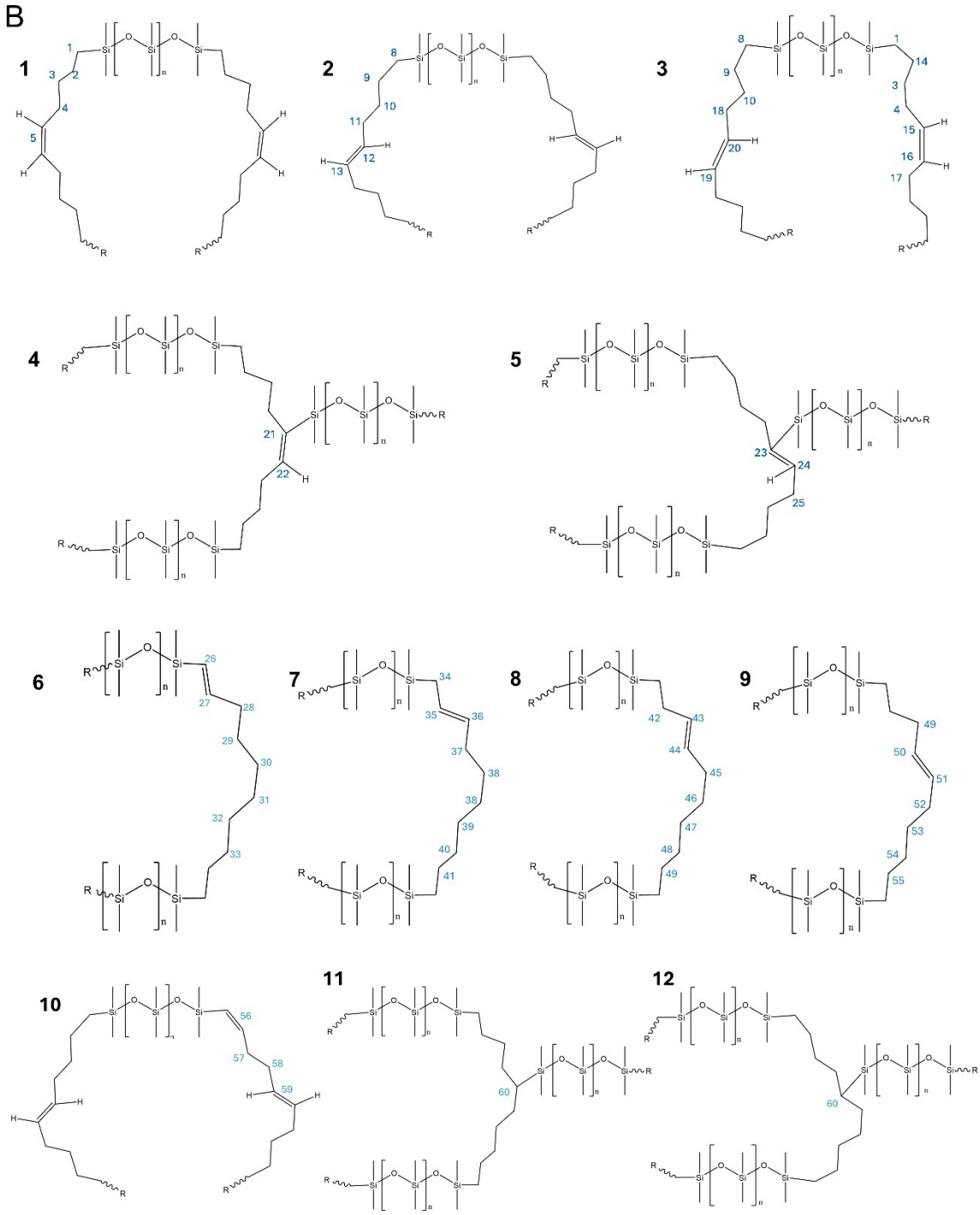
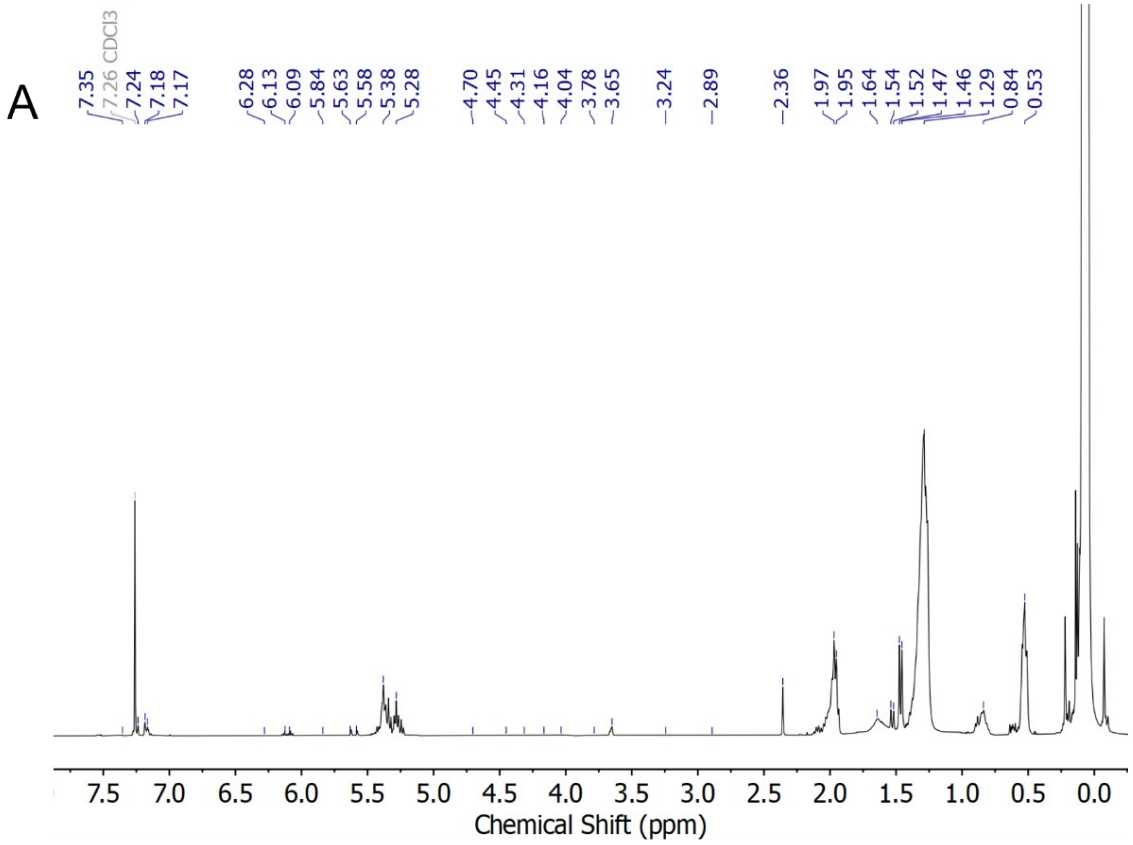


Figure S4. A) Solid-state ^{13}C-NMR spectra of the elastomer DMS-DT-H11 prepared with an r-value of 1. B) Identified structures within the elastomer network.

Table S5. Swelling characteristics of the DMS-DT-H11 and DMS-DT-H21 networks prepared with a stoichiometric imbalance, r = Si-H/C=C, of 1 and 1.1.

Sample	Sol fraction (%)	Gel fraction (%)	Swelling ratio
DMS-DT-H11 (r=1.1)	9.4	90.6	6.9
DMS-DT-H21 (r=1.1)	9.9	90	6.9
DMS-DT-H11 (r=1.0)	21.3	78.7	11
DMS-DT-H21 (r=1.0)	24.5	75.5	24

A


7.35
7.26 CDCl3
7.24
7.18
7.17
6.28
6.13
6.09
5.84
5.63
5.58
5.38
5.28
4.70
4.45
4.31
4.16
4.04
3.78
3.65
3.24
2.89
2.36
1.97
1.95
1.64
1.54
1.52
1.47
1.46
1.29
0.84
0.53
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical Shift (ppm)

B

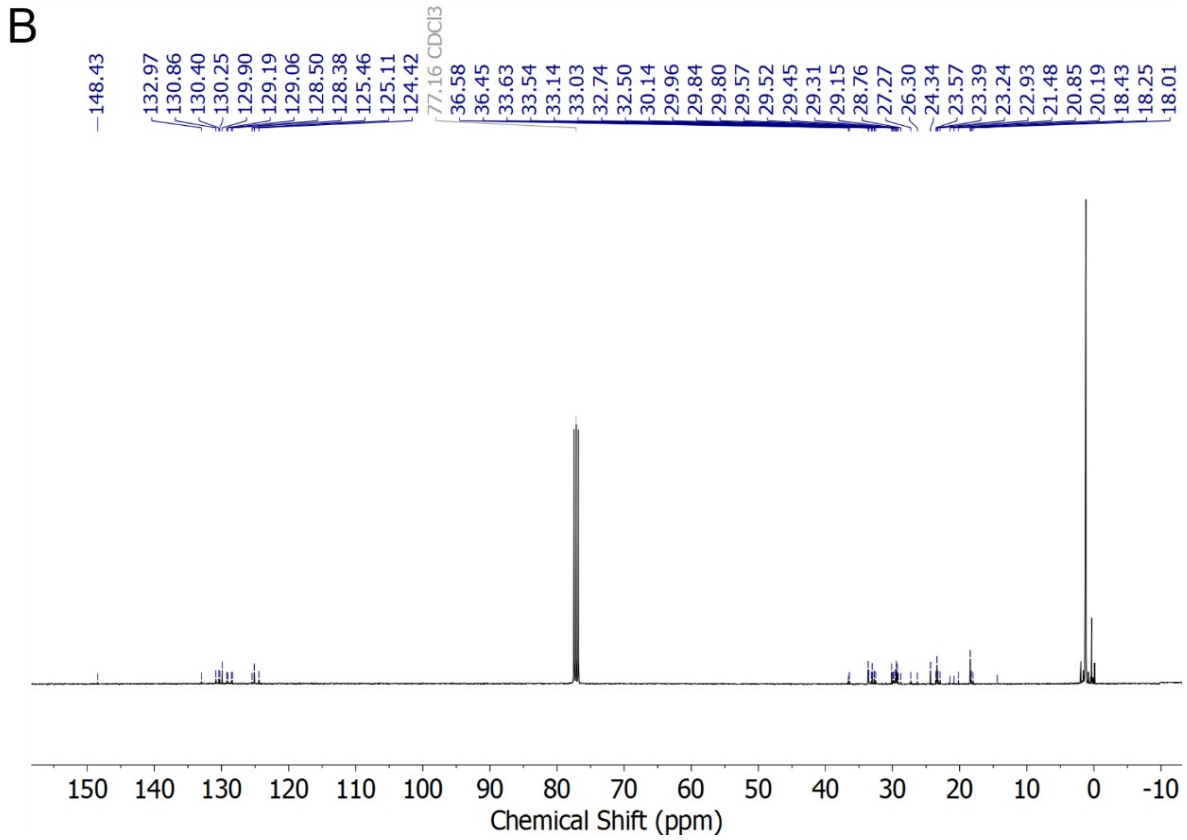

148.43
132.97
130.86
130.40
130.25
129.90
129.19
129.06
128.50
128.38
125.46
125.11
124.42
77.16 CDCl3
36.58
36.45
33.63
33.54
33.14
33.03
32.74
32.50
30.14
29.96
29.84
29.80
29.57
29.52
29.45
29.31
29.15
28.76
27.27
26.30
24.34
23.57
23.39
23.24
22.93
21.48
20.85
20.19
18.43
18.25
18.01
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

Figure S5. A) ^{1}H-NMR spectrum of the sol fraction extracted from the DMS-DT-H11 network. B) ^{13}C-NMR spectrum of the sol fraction extracted from the DMS-DT-H11 network.

The ^{1}H-NMR (400 MHz, $CDCl_3$, δ_H) of the sol fraction (Fig. S5a) shows the resonances at 0.54 ppm (Si-C*H*$_2$ (1 + 8)), 0.84 ppm (Si-C*H*$_2$- (1); C*H*$_3$-CH= (RD-PDV)), 1.29 ppm (C*H*$_2$-C*H*$_2$ (2 + 3 + 9 + 10), Si-C*H*$_2$- (8)), 1.46 – 1.47 ppm (CH_2-C*H*$_2$ (42)), 1.52 ppm (CH_2-C*H*$_2$ (33)), 1.54 ppm (CH_2-C*H*$_2$ (40)), 1.64 ppm (IS-PDV, Si-C*H*$_2$-C*H*$_2$ (49)), 1.95 ppm (C*H*$_2$-CH= (4 + 11 + 18 + 49 + 52)), 1.97 ppm (=CH-C*H*$_2$ (28 + 38 + 42 + 45)), 2.89 ppm (=CH-C*H*$_2$-CH= (IS-PDV)), 4.45 ppm (CH_3-C*H*=CH (IS-PDV)), 4.70 ppm (CH_3-C*H*=CH (IS-PDV)), 5.28 ppm (C*H*=C*H* (5 +12 +13)), 5.38 ppm (C*H*=C*H* (20 + 15 + 27 + 43 + 44 + 22 + 24)), 5.63 – 5.84 ppm (C*H*=C*H* (5)), 6.09 – 6.13 ppm (C*H*=C*H* (12 + 13)), 7.17 – 7.18 ppm (C*H*=C*H* (56 + 59)), 7.24 ppm (C*H*=C*H* (26 + 27)).

The ^{13}C-NMR (400 MHz, $CDCl_3$, δ_C) of extracted sol fraction (Fig. S5b) has resonances at 18.01 ppm (1 (*structure 6*)), 18.25 ppm (1), 18.43 ppm (8), 20.19 ppm (41 + 49 + 55), 22.93 ppm (2), 23.39 ppm (9), 24.34 ppm (42), 26.30 ppm (3), 27.27 ppm (4), 28.76 ppm (58), 29.15 ppm (57), 29.31 ppm (39 + 47), 29.45 ppm (53), 29.52 ppm (29), 29.57 ppm (38), 29.80 ppm (30 + 31), 29. 84 ppm (38), 29. 96 ppm (45 + 46), 30.14 ppm (34 + 38), 30.81 ppm (28), 31.45 ppm (IS-PDV), 32.50 (10), 32.74 ppm (17 + 40 +52), 33.03 ppm (48 + 54), 33.14 ppm (11), 33.54 – 33.63 ppm (18), 36.45 ppm (25), 124.42 ppm (27), 125.11 ppm (35), 125.46 ppm (IS-PDV), 128.38 ppm (36 + 43 + 50), 129.19 ppm (5 + 15), 129.90 ppm (56), 130.25 ppm (26), 130.40 ppm (13 + 59), 130.86 ppm (12 + 20 + 44 + 56), 132.97 ppm (22 + 25 + 24), 148.43 ppm (21 + 23).

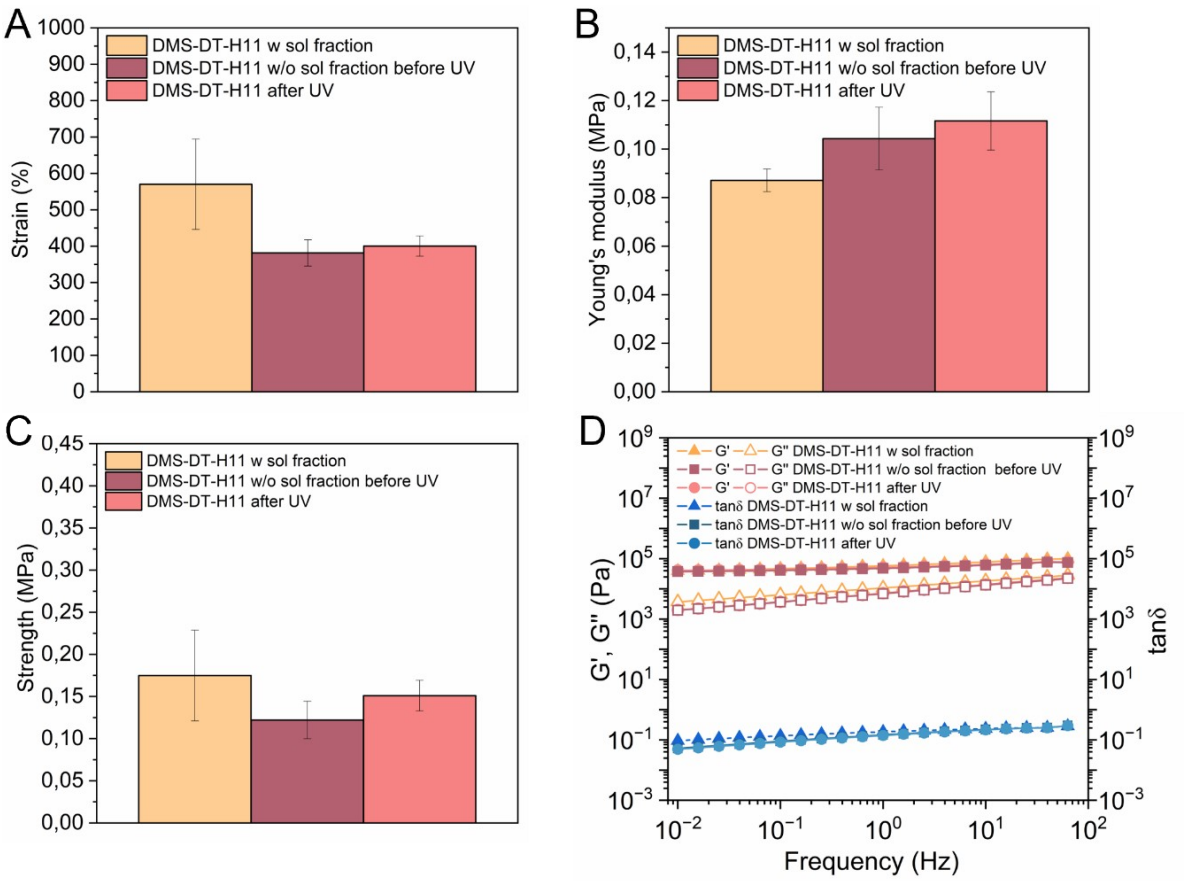


Figure S6. Comparison of the mechanical and rheological properties of a DMS-DT-H11 network with a stoichiometric imbalance, r, of 1 before (w sol fraction) and after (w/o sol fraction) swelling in THF for 24 h and after 12 minutes UV-Vis treatment A) tensile strain, B) Young's modulus, C) tensile strength, and D) storage modulus, loss modulus, and tan δ. All properties reported at room temperature.